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1  
2           CHEMICAL IMAGING OF A LITHOGRAPHIC PRINTING PLATE

## 3           CROSS REFERENCE TO RELATED APPLICATIONS

4           This application is a continuation-in-part of U.S. Application Serial Nos. 09/941,304 and  
5   09/941,323, both filed August 29, 2001, which are, in turn, divisionals of U.S. Application Serial  
6   No. 09/566,453, filed May 8, 2000. This application also claims benefit of U.S. Provisional  
7   Application Serial Nos. 60/281,742, 60/281,743 and 60/281,744, all filed on April 3, 2001.

## 8           BACKGROUND OF THE INVENTION

9           This invention relates to a process for imaging a lithographic printing plate and more  
10   particularly to a process using an ink jet printer to imagewise apply an insolubilizing chemical to  
11   a plate coating which comprises photosensitive compounds or their reaction products.12          In the art of lithographic printing it is generally required that one or more lithographic  
13   printing plates be mounted on a printing press. The lithographic printing plate is characterized  
14   by having on its printing surface oleophilic ink receiving areas in the form of the image to be  
15   printed, and hydrophilic water receiving areas corresponding to the other, non-printing areas of  
16   the surface. Because of the immiscibility of oil-based lithographic inks and water, on a well-  
17   prepared printing plate, ink will fully coat the oleophilic areas of the plate printing surface and  
18   not contaminate the hydrophilic areas. The operating press brings the inked plate surface into  
19   intimate contact with an impression cylinder or elastic transfer blanket that transfers the ink  
20   image to the media to be printed.21          Traditionally, a lithographic plate is photographically imaged. The plate substrate is  
22   most commonly aluminum, from 5 to 12 mils thick, treated so that the printing surface is  
23   hydrophilic, although treated or untreated plastic or paper substrates can also be used. The

1 substrate is coated with a solution of a photosensitive composition that is generally oleophilic.  
2 Upon drying, the coating layer thickness is commonly about 1 to 3 microns thick. A printing  
3 plate with such a photosensitive coating is called "presensitized" (PS). Both negative and  
4 positive working photosensitive compositions are used in PS lithographic plates. In a negative  
5 plate, light exposure insolubilizes the coating, so that on development the only parts of the  
6 coating that aren't removed are the light imaged areas. The reverse is the case in a positive  
7 plate. Light exposure solubilizes the coating; on development the coating is only removed in the  
8 areas that are light imaged. In an image reversal process, a positive plate is "blanket exposed" or  
9 "flood exposed", i.e., the entire plate is light exposed without any intervening mask or other  
10 means for imaging, and imaged in a separate step which can be performed before or after the  
11 blanket exposure step. By this image reversal process, a positive plate can be negatively imaged.  
12 The aluminum substrate can be treated to make it hydrophilic either prior to the application of  
13 the photosensitive composition or at the time the non-image areas of the coating are removed in  
14 a development step. Such a process in which a pre-coated lithographic plate is prepared for  
15 press by removing exclusively either the imaged or non-imaged coating in a development step is  
16 called a subtractive process; a pre-coated plate having a coating which is at least partially  
17 removed in a development step is known as a subtractive plate.

18 Photosensitive compositions used in positive lithographic plates are well known. They  
19 are comprised primarily of alkali soluble resins and o-quinone diazide sulfonic acid esters or  
20 amides. In addition dyes or colored pigments, indicator dyes, plasticizers and surfactants can  
21 also be present. The ingredients are typically dissolved in organic solvents and are coated onto  
22 the substrate. Upon drying a thin film or coating is produced.

1 Alkali soluble resins useful in positive plates are well known and include phenol-  
2 formaldehyde resins, cresol-formaldehyde resins, styrene-maleic anhydride copolymers, alkyl  
3 vinyl ether-maleic anhydride copolymers, co-or ter-polymers that contain either acrylic or  
4 methacrylic acids and poly(vinyl phenol). U.S. Pat. No. 4,642,282 describes an alkali soluble  
5 polycondensation product that is also useful as the resin component in positive plates.

6 The o-quinone diazide compounds include o-benzoquinone diazides, o-naphthoquinone  
7 diazides and o-anthraquinone diazides. O-quinone diazide compounds useful in positive plates  
8 are well known and are described in detail in Light Sensitive Systems by J. Kosar, p.339-352.  
9 They are further described in U.S. Pat. Nos. 3,046,118; 3,046,119; 3,046,120; 3,046,121;  
10 3,046,122; 3,046,123; 3,148,983; 3,181,461; 3,211,553; 3,635,709; 3,711,285 and 4,639,406  
11 incorporated in entirety herein by reference.

12 Such positive plates are sensitive to light in the wavelength range of from about 290 to  
13 500nm. When used in the standard manner, photo-exposure causes the alkali insoluble o-  
14 quinone diazide of the positive plate to be converted into an alkali soluble carboxylic acid. Upon  
15 subsequent treatment with a developer, which is a dilute aqueous alkaline solution, the exposed  
16 parts of the coating are removed. The unexposed coating is alkali insoluble, because the o-  
17 quinone diazide is unaffected by the developer, and remains on the substrate.

18 Traditionally, lithographic plates are imaged by photographic transfer from original  
19 artwork. This process is labor-intensive and costly. Hence with the advent of the computer  
20 engendering a revolution in the graphics design process preparatory to printing, there have been  
21 extensive efforts to pattern printing plates, in particular lithographic printing plates, directly  
22 using a computer-controlled apparatus called a platesetter that is supplied with digital data  
23 corresponding to the image to be printed. A platesetter has the capability to supply an image

1 forming agent, typically light energy or one or more chemicals, to a plate according to various  
2 patterns or images as defined by digital data, i.e., to imagewise apply an image forming agent.  
3 Specially manufactured lithographic plates may be required for certain types of platesetters.  
4 Such a combination of a computer-controlled platesetter and the proprietary plates used with  
5 them along with developer solutions and any other materials or apparatuses necessary to prepare  
6 the plates for printing is known as a computer-to-plate (CTP) system.

7 Heretofore, many of the new CTP systems have been large, complex, and expensive.  
8 They are designed for use by large printing companies as a means to streamline the prepress  
9 process of their printing operations and to take advantage of the rapid exchange and response to  
10 the digital information of graphic designs provided by their customers. Many of the new CTP  
11 systems use light sources, typically lasers, to directly image PS plates. But using lasers to image  
12 plates is very expensive, because the per-unit cost of the lasers is high and because they require  
13 sophisticated focusing optics and electronic controls. If because of the cost only a single laser is  
14 used, then time becomes a constraint because of the necessity of raster scanning. There remains  
15 a strong need for an economical and efficient CTP system for the many smaller printers who  
16 utilize lithographic printing.

17 In recent years, ink jet printers have replaced laser printers as the most popular  
18 hard copy output printers for computers. Ink jet printers have several competitive advantages  
19 over laser printers. One advantage is that it is possible to manufacture an array of 10's or even  
20 100's of ink jet nozzles spaced very closely together in a single inexpensive print head. This  
21 nozzle array manufacturing capability enables fast printing ink jet devices to be manufactured at  
22 a much lower cost than laser printers requiring arrays of lasers. And the precision with which  
23 such a nozzle array can be manufactured and the jetting reliability of the incorporated nozzles

1 means that these arrays can be used to print high quality images comparable to photo or laser  
2 imaging techniques. Ink jet printers also are increasingly being used for prepress proofing and  
3 other graphic arts applications requiring very high quality hard copy output.

4 In spite of the large and rapidly growing installed base of ink jet printers for hard copy  
5 output, ink jet printing technology is not commonly used in CTP systems. There are many  
6 challenging technical requirements facing the practitioner who would design such an ink jet  
7 based CTP system as can be seen in the prior art. A first requirement is that the ink jet ink used  
8 to image the printing plate be jettable, able to form ink drops of repeatable volume and in an  
9 unvarying direction. Further, for practical commercial application, the ink must have a long  
10 shelf life, in excess of one year or more. US Pat. No. 5,970,873 (DeBoer et al) describes the  
11 jetting of a mixture of a sol precursor in a liquid to a suitably prepared printing substrate. But  
12 any ink constituents of limited solubility will render unlikely the practical formulation of a  
13 jettable, shelf-stable ink. Similar problems exist in US Pat. No. 5,820,932 (Hallman et al) in  
14 which complex organic resins are jetted, and US Pat. No. 5,738,013 (Kellet) in which marginally  
15 stable transition metal complexes are jetted. In US 6,187,380 B1 (Hallman et al) and 6,131,514  
16 (Simons), inks comprising acrylic resins such as trimethylolpropanetriacrylate and  
17 poly(ethylene-co-acrylic acid, sodium salt), are jetted. While it may be possible to make such a  
18 ink formulation work for the purposes of a short term experiment, it would almost certainly clog  
19 the nozzles of an ink jet printhead were the ink allowed to remain in the printer for the weeks or  
20 more that would be a requirement of practical commercial use.

21 Another requirement is that to be of wide utility, the ink jet based CTP system should be  
22 able to prepare printing plates with small printing dots, approximately 75 microns in diameter or  
23 smaller, so that high resolution images can be printed. Ink jet printers can produce such small

1 dots, but of those having substantial commercial acceptance, only ink jet printers employing  
2 aqueous-based inks are practically capable of printing such small dots. Thus the systems  
3 described in US Pat. Nos. 4,003,312 (Gunther), 5,495,803 (Gerber), 6,104,931 (Fromson et al),  
4 and 6,019,045 (Kato) which use solvent-based hot melt inks will not allow the preparation of the  
5 high resolution printing plates necessary for printed images of high quality. Further, hot melt  
6 type inks typically freeze on top of the imaged media rather than penetrate into it. This would  
7 prevent intimate mixing between potential reactants in the inks and corresponding potential  
8 reactants in a PS plate coating. It is also required that the prepared printing plates be rugged,  
9 capable of sustaining press runs of many thousands of impressions. The waxes used in the hot  
10 melt inks described in US Pat. No. 6,019,045 (Kato) and 4833486 (Zerillo) would wear out in  
11 such a long press run.

12 Another requirement of a successful ink jet based CTP system is that a mature plate  
13 technology is to be preferred. Although the prior art demonstrates that it is not obvious to do so,  
14 it greatly simplifies the development of an ink jet CTP system to be able to use commercially  
15 available, widely accepted PS plates. There are many tradeoffs in the manufacture of  
16 commercially practical lithographic plates. They must be highly sensitive to the imaging process  
17 and yet thermally stable, stable in high humidity storage environments and yellow light, resistant  
18 to fingerprints, of minimal toxicity and environmentally benign, easily developed in that small  
19 dots are quantitatively resolved without dot blooming using developers that are of minimal  
20 toxicity and environmentally benign, able to sustain long press runs, manufacturable at a low  
21 cost per square foot, and many other practical requirements. US Pat. No. 5,695,908 (Furukawa)  
22 describes a process for preparing a printing plate comprising a new plate coating containing a  
23 water-soluble polymer that becomes water-insoluble in contact with a metal ion in a solution

1 jetted imagewise. But such a new plate coating is unlikely to meet the wide array of constraints  
2 on a successful plate technology. U.S. Pat. No. 5,466,653 (Ma et al) describes a plate coating  
3 that requires an impractically high reaction temperature for imaging. US Pat. No. 6,025,022  
4 (Matzinger) describes a new plate coating on a glass substrate that would be unlikely to find  
5 wide acceptance

6 To use an ink jet printer in a positive imaging process is impractical because in typical  
7 printing, the area of a plate containing images such as text, graphics, and line work, is much less  
8 than the non-image containing area of the plate. Thus to be able to image widely accepted  
9 positive plates with a negative imaging ink jet process is a unique, surprising, and valuable  
10 result.

11 Positive plates based on o-naphthoquinone diazide sulfonic acid esters can be modified  
12 by the incorporation of alkaline materials to obtain image reversal. US Patent No. 4,104,070  
13 describes the use of imidazolines; US Patent No. 4,196,003 describes the addition of secondary  
14 and tertiary amines and US Patent No. 4,356,254 describes the addition of basic carbonium dyes  
15 to produce image reversal. The sequential steps for this image reversal process are imagewise  
16 light exposure, heat treatment, blanket light exposure and alkaline development. Those coatings  
17 have never achieved any commercial success, which is attributed to the adverse effect on the  
18 properties of the coating by the addition of the alkaline materials. US Patent No. 4,007,047  
19 describes image reversal of a positive resist by a modification of the photoimaging process.  
20 After imagewise exposure, the resist coating is subjected to an acid treatment by immersion into  
21 a heated acid solution, which after a water rinse and drying steps produces a negative image after  
22 blanket light exposure and development.

23

## 1    SUMMARY OF THE INVENTION

2       The present invention provides a process for preparing PS lithographic plates for printing  
3       by employing an ink jet printhead to imagewise apply an insolubilizing chemical. In one aspect  
4       of the invention, the steps comprise:

- 5                 (a) providing an on-press developable PS plate;  
6                 (b) imagewise applying an insolubilizing chemical to the plate coating;  
7                 (c) heating the plate;  
8                 (d) mounting the plate on a printing press; and  
9                 (e) operating the press.

10      In another aspect of the invention, the steps comprise:

- 11                 (a) providing a positive plate;  
12                 (b) blanket exposing the plate;  
13                 (c) imagewise applying an insolubilizing chemical to the plate coating;  
14                 (d) heating the plate; and  
15                 (e) developing the plate.

16      In yet another aspect of the invention, the steps comprise:

- 17                 (a) providing a plate with a coating;  
18                 (b) imagewise applying an insolubilizing chemical to the coating;  
19                 (c) heating the plate; and  
20                 (d) washing the plate with a developing solution.

21

22         Accordingly, there are several objects and advantages of the present invention. An object  
23         of the present invention is that it is easily embodied in a practical, reliable, and inexpensive ink-

1 jet-based CTP system with minimal constraints on the formulation of the imaging fluid, and in  
2 that widely-available, commercially-accepted lithographic plates with desirable aluminum  
3 substrates and their corresponding commercially-accepted development solutions can be used  
4 without modification. A plate prepared by the present invention is functionally similar to a plate  
5 prepared by photographic imaging, with a potential long run life but without the complexity,  
6 cost, or waste of a film negative. The plate can be prepared quickly, in that fewer steps are  
7 required and in that a speedy ink jet printer can be employed, and yet the plate image is of high  
8 resolution, enabling high quality 4-color printing. Further, the plate thus prepared is storage  
9 stable, little subject to contamination in its hydrophilic areas and can be used on a wide variety  
10 of commercially available and accepted printing presses. The formulation of the insolubilizing  
11 fluid is flexible and can be simple, inexpensive to manufacture, environmentally safe, and non-  
12 toxic. Water can be used as a vehicle resulting in small drops that easily penetrate PS coatings  
13 facilitating intimate mixing of the insolubilizing chemical with the reactive constituents of the  
14 coating. The chemicals used in the fluid in this invention that enable insolubilization to occur on  
15 negative and photo-exposed positive plates cover a wide range of materials. That such a simply  
16 and flexibly formulated ink can be jetted in very small diameter drops to produce high resolution  
17 images on conventional and widely accepted positive and negative working plates is a unique  
18 and surprising result. That commercially available positive plates can be economically and  
19 efficiently imaged by ink jet in a negative working process is a unique and surprising result.  
20 Printers already using positive plates for printing requiring light imaging exposure can now use  
21 efficient and economical ink jet negative imaging without having to switch plate types.

22 Still other objects and advantages will become apparent from the claims, and from a  
23 consideration of the ensuing detailed description of the invention.

1 BRIEF DESCRIPTION OF THE DRAWINGS

2 FIG. 1 is a cross-sectional perspective view of a conventional developing processor in a  
3 preferred configuration according to the invention.

4 FIG. 2 is a block diagram flowchart depicting the process in which an on-press developable  
5 printing plate is imaged by ink jet, developed on press, and then used in a printing operation.

6 FIG. 3 is a block diagram flowchart depicting a process in which an image reversal technique is  
7 used to negatively image a presensitized printing plate by ink jet.

8 FIG. 4 is a continuation of the flowchart of Fig. 3.

9 FIG. 5 shows the essential elements of a computer-to-press system comprising an ink jet  
10 printhead enabling in situ imaging of a printing plate mounted on press.

11

12 DETAILED DESCRIPTION OF THE INVENTION

13 The invention comprises a subtractive process for preparing a printing plate for press by  
14 imagewise applying an insolubilizing chemical to a coated plate, completing the insolubilization  
15 reaction by heating if necessary, and washing the plate with a developing solution. The  
16 insolubilizing chemical undergoes a chemical reaction with, or facilitates a chemical reaction in,  
17 the plate coating, making the reacted coating insoluble to a developing solution in which the  
18 unreacted coating is soluble. In the case of an on-press developable plate, the developing step is  
19 effectively performed using the working fluids of the press, i.e., the press fountain solution and  
20 ink.

21 A computer-to-plate system according to the invention preferably comprises an ink jet  
22 printer (IJP) and a developing processor. To facilitate accurate imaging of the plate, the paper-  
23 handling or substrate-handling subsystem of ink jet printer should have a short, straight paper

1 path. A printing plate is generally stiffer and heavier than the paper or media typically used in  
2 commercially available ink jet printers. If the plate fed into the printer mechanism must bend  
3 before or after being presented to the imaging print head, then the movement of the plate through  
4 the printer may not be as accurate as the media for which the printer was designed. The most  
5 preferred EPSON Stylus Color 3000 has such a short, straight paper path. A platen is preferably  
6 placed at the entrance to the paper feed mechanism. The platen preferably has a registration  
7 guide rail and supports the plate as it is pulled into the printer by the feed mechanism, facilitating  
8 the accurate transport of the plate under the imaging print head.

9           In the most preferred embodiment, the IJP used is a commercially available drop-on-  
10 demand printer capable of printing small ink drops having volumes no larger than 8 picoliters (8  
11 pl) such as the EPSON Stylus Color 3000 ink jet printer available from Epson America, Inc.,  
12 Long Beach, CA. However, the great flexibility available to the practitioner in formulating an  
13 insolubilizing fluid according to the invention means that a well-performing jettable solution can  
14 be formulated such that the print head of almost any ink jet printer will be able to form regular  
15 drops with good reliability.

16           Because the powerful solvating capability of water, aqueous ink jet drops typically  
17 penetrate the imaged media. Without being bound by theory, it is believed this may be  
18 important to the invention because it is probably necessary for the insolubilizing chemical to be  
19 brought into intimate contact with the reactive constituents of the plate coating to effect  
20 insolubilization. Although water is the most preferred fluid vehicle, it is also possible to use  
21 other penetrating solvents such as methyl ethyl ketone, ethyl acetate, ethyl lactate, dimethyl  
22 formamide, acetone, simple alcohols, and other like chemicals or mixtures of such chemicals.  
23 Typically, the vehicle would comprise 30 to 99 percent of the imaging fluid.

1           In one embodiment of the invention, the insolubilizing agent comprises pH-elevating  
2   agents typically of low molecular weight such as sodium carbonate, sodium bicarbonate, lithium  
3   carbonate, lithium hydroxide, sodium hydroxide, potassium hydroxide, sodium  
4   tetraboratedecahydrate, sodium pyrophosphatedecahydrate, sodium phosphate, sodium  
5   metasilicate, or amines such as ethanolamine, diethanolamine, triethanolamine, ethylamine,  
6   propylamine, butylamine, imidazolines, substituted imidazolines such as 1-hydroxyethyl-2-  
7   cocylimidazoline, 1-hydroxyethyl-2-caprylimidazoline, 1-hydroxyethyl-2-oleylimidazoline, and  
8   1-hydroxyethyl-2-tall oil imidazoline, tall-oil fatty acid-diethylenetriamine imidazoline,  
9   imidazoles, substituted imidazoles, amino amides, polyamines, or mixtures of such chemicals.

10          The pH range of the imaging fluid is between 7.5 and 14, and more preferably from about 8.0 to  
11       12.5.

12          In another embodiment of the invention, the insolubilizing agent comprises one or more  
13   amine salts prepared by the reactions of amines including imidazolines with either acids or with  
14   quaternarizing agents. Examples of such amine salts are ammonium acetate, acetates of ethyl  
15   amine, propyl amine and triethanol amine and related salts, 1-hydroxyethyl-2-cocylimidonium  
16   sulfate, 1-hydroxyethyl-2-cocylimidonium acetate, imidonium acetate, 1-hydroxyethyl-2-  
17   caprylimidonium hydroxyacetate, 1-hydroxyethyl-2- oleylimidonium phosphate, isostearyl  
18   ethylimidonium ethosulfate, acetates of amino amides and related compounds. The  
19   insolubilizing agent typically comprises from 0.05 to 7 percent of the fluid, but in specific  
20   instances can comprise as much as 25% of the fluid.

21          For reliable jetting, and so that during idle periods the fluid does not dry out in the ink jet  
22   nozzle causing it to clog, a humidifying co-solvent may be added to the insolubilizing fluid. The  
23   co-solvent can be a polyhydric alcohol such as glycerin, ethoxylated glycerin, ethylene glycol,

1 diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, or trimethylol  
2 propane, other high boiling point liquids such as pyrrolidone, methylpyrrolidone, or triethanol  
3 amine, other simple alcohols such as isopropyl alcohol or tertiary butyl alcohol, or mixtures of  
4 such solvents. When used, the co-solvent would typically comprise 5 to 70 percent of the fluid.

5 A dye compatible with the insolubilizing agent can be added to the fluid at a level of a  
6 few percent to enhance the visibility of the latent image. The insolubilizing fluid may contain  
7 one or more surfactants or wetting agents to control the surface tension of the ink, enhancing  
8 jettability, and to control the spread and penetration of the drop on the coated plate. The  
9 surfactants and wetting agents may include Surfynol 104, Surfynol 465, Surfynol FS-80,  
10 Surfynol PSA-216, Dynol 604, Triton X-100, and similar chemicals or mixtures of similar  
11 chemicals. When used, surfactants and wetting agents typically comprise 0.001 to 10 percent of  
12 the fluid.

13 The insolubilizing fluid may also contain one or more biocides to prolong the shelf life of  
14 the fluid. Suitable biocides include for example Proxel GXL, Sodium Omadine, Dowicil,  
15 GivGuard DXN, and similar chemicals or mixtures of such chemicals. When used, the biocide  
16 would typically comprise 0.1 to 3 percent of the ink. If the pH of the insolubilizing fluid is over  
17 10, it is not necessary to use a biocide and this is preferred.

18 A typical formulation for an insolubilizing fluid comprises:

19	Water with sufficient amount of insolubilizing agent	70%
20	Co-solvent	26%
21	Dye	3%
22	Surfactant	1%

1        Imagewise application of the insolubilizing fluid onto the plate coating using an ink jet  
2        printhead results in a latent image on the plate. To complete preparation for use, it is then  
3        necessary to develop the imaged plate. In one embodiment of the invention, it is preferable to  
4        use a conventional developing processor. A most preferred processor configuration is illustrated  
5        in Fig 1. An imaged plate is conveyed first through a hot air drying section 10, second through a  
6        pre-heat oven 12, third through a development station 14 where the appropriate developing  
7        solution is poured on the plate and the solubilized coating removed. Fourth, the plate is  
8        conveyed through a rinse section 16, and finally, fifth through a post bake oven 18. The plate is  
9        then ready to be used on press.

10        In another embodiment of the invention, illustrated in Fig. 2, an on-press developable plate is  
11        imaged. In this embodiment, after imaging of the subtractive plate 20 by an ink jet printer 22, no  
12        conventional development of the latent image 26 is required. Instead, the plate is first heated in  
13        an oven 24 to dry the image and, without being bound by theory, complete the insolubilization  
14        reaction. Second, the plate is mounted on the plate cylinder of a conventional offset lithographic  
15        press 28. Third, the latent image is developed by operating the press such that the plate cylinder  
16        is rotated and the working fluids of the press, i.e., the press ink and fountain solution, are applied  
17        to the plate coating. The plate is then ready to be used to print images on paper or other media  
18        30 by the normal operation of the press.

19

20        Positive Plate

21        In this aspect of the invention, as illustrated in Figs. 3 and 4, a method for preparing a  
22        positive plate for press by an image reversal process comprises the steps of:

23              a)        providing a conventional subtractive positive plate. A side view is shown 40.

- 1           b)    Blanket exposing the plate coating using a light source 42. A side view of the  
2                 exposed plate is shown 44. A top view of the exposed plate is shown 46.  
3           c)    Applying imagewise an insolubilizing chemical to the coating preferably  
4                 using an ink jet printer 48;  
5           d)    heating the plate in an oven 50. The latent image on the plate is indicated 52.  
6           e)    Developing the plate in a conventional processor 54. The plate is then ready  
7                 for use 56.

8

9           The positive plate can be blanket light exposed just before the plate is chemically  
10          imaged. The IJP can also be expanded to include a light exposure attachment placed on the  
11          printer before the imaging printhead. In this expanded system, the blanket light exposure and  
12          chemical imaging steps can be performed in a continuous operation. The plate can also be  
13          blanket light exposed at the time of manufacture by including a light exposure step after drying  
14          and before packaging. The latter procedure would eliminate a processing step for the user.

15          Preferred light sources that can be used in the blanket light exposure step are those that emit light  
16          in the wavelength range of from about 290 to 500 nm. Suitable light sources are carbon arcs,  
17          mercury lamps, fluorescent lamps and metal halide lamps.

18          After blanket exposure, a latent image is created in the coating of the plate by imagewise  
19          application of a chemical that causes the affected area of the coating to become insoluble in the  
20          developing solution. It is simplest and preferred to formulate a fluid solution comprising the  
21          insolubilizing chemical, and to use an ink jet printer for the imagewise application of the  
22          insolubilizing solution. As described above, effective insolubilizing agents can be bases  
23          including amines, and amine salts.

1        According to this invention, without being bound by theory, when the positive plate is  
2        first given a blanket light exposure the o-quinone diazide compound is converted into a  
3        carboxylic acid that renders the coating soluble in dilute aqueous alkaline solutions. An  
4        insolubilizing fluid is then imagewise jetted onto the light exposed plate followed by a brief heat  
5        treatment of the plate. During the heat treatment step, decarboxylation is believed to occur only  
6        in the areas on the plate that were jetted with fluid. In these decarboxylated areas, the coating is  
7        no longer soluble in dilute aqueous alkaline solutions such as typical positive plate developing  
8        solutions. When treated with such dilute alkaline solutions in the development step, all the  
9        coating is removed from the plate except in the areas where the fluid has been jetted. A reverse  
10      image is thus produced. The plate is then ready to be mounted and used in a conventional press.

11       Note that this process, termed an "image reversal" process as used herein is somewhat  
12      different than the typical light-based image reversal processes used in photolithographic  
13      applications in that it is usually necessary to follow the imagewise application of the chemical by  
14      a heating step. Further, the imaging step is carried out after the blanket exposure step rather than  
15      before because the carboxylic acids in the coating need to be created via the blanket exposure  
16      step before they can be decarboxylated in the imaging and heating steps. In a prior art  
17      application of image reversal for the purpose of imaging printing plates described in US  
18      4,927,741, the blanket exposure step follows the heat treatment, which reduces the effectiveness  
19      of the blanket exposure step in solubilizing the non imaged areas of the coating. In this patent, a  
20      cumbersome method to minimize this problem is described which requires that the blanket  
21      exposure step be carried out while the coating is submerged under water.

22       The concentration of the active ingredient, the decarboxylating agent, in the  
23      insolubilizing fluid can range from about 0.05 to 20 percent or preferably from about 0.1 to 3.5

1 percent. A dye compatible with either the alkaline materials or the amine salts can be added to  
2 the fluid at a level of a few percent to enhance the visibility of the latent image.

3         After application of the insolubilizing chemical, the plate is heated for the purpose of  
4 completing the insolubilization reaction. The extent of the heat treatment required is dependent  
5 on the particular o-quinone diazide that is incorporated in the coating. A coating made from an  
6 o-quinone diazide having the sulfonic acid ester group in the same ring as the quinone diazide  
7 group requires a less vigorous heat treatment than one where the two groups aren't in the same  
8 ring. If the plate coating is made from an o-naphthoquinone -1,2-(diazide-2)-5-sulfonic acid  
9 ester, it is preferably heated to between 55 to 130C for from 15 seconds to 10 minutes or most  
10 preferably from about 90 to 110C for 1 to 2 minutes. If the plate coating is made from an o-  
11 naphthoquinone-1,2-(diazide-2)-4-sulfonic acid ester, it is preferably heated to between 40  
12 to 110C for from 3 seconds to 5 minutes or most preferably from about 50 to 60C for from 30 to  
13 90 seconds. The maximum heat treatment that can be applied is limited by the heat treatment  
14 conditions of time and temperature that would cause decarboxylation to occur in the non-  
15 chemically imaged areas of the coating. After heating, the plate is developed either by hand or  
16 preferably with a conventional developing processor using a conventional developing solution to  
17 produce the image.

18         As described above, the insolubilizing fluid applied to the light exposed positive plate is  
19 believed to react by decarboxylating the carboxylic acid that forms from the o-quinone diazide  
20 during photo-exposure. The elimination of the carboxylic group in one of the chemicals in the  
21 lithographic plate coating changes its alkaline solubility from soluble to insoluble. When the  
22 plate is processed by the developing solution, a dilute aqueous alkaline solution, the unprinted

1 areas of the coating are quantitatively dissolved, leaving the hydrophilic-treated aluminum bare,  
2 and the printed areas coating are apparently undisturbed.

3       The concentration of the o-quinone diazide in the positive plate can vary over wide  
4 limits. In general, the proportion is 5 to 50 percent and more preferably between 20 and 40  
5 percent, based upon weight. The concentration of the resin component is from about 50 to 95  
6 percent and more preferably from 60 to 80 percent. The resin component can be used without  
7 any addition of a separate o-quinone diazide compound if the resin has o-quinone diazide groups  
8 covalently bonded to it. The coating thickness of the positive coating can range from about 0.4  
9 to 4 grams/square meter. The preferred o-quinone diazides are naphthoquinone-1,2-(diazide-2)-  
10 5-sulfonic acid esters and naphthoquinone -1,2-(diazide-2)-4-sulfonic acid esters. They are  
11 prepared by the reactions of the corresponding sulfonyl chlorides with alcohols and phenols.  
12 The preferred phenolic compounds for these reactions are cresol-formaldehyde resins, di, tri,  
13 tetra, and poly hydroxy aromatics either unsubstituted or substituted with other groups. Some  
14 examples of such phenolic compounds are resorcinol, phloroglucinol, 2,3,4-  
15 trihydroxybenzophenone and tetrahydroxybenzophenone.

16       The developer used for this invention is similar to the typical dilute aqueous alkaline  
17 solutions used on positive plates. They preferably have a pH of 11 or higher. Illustrative of the  
18 various bases that can be used to adjust the alkalinity of the developer are sodium hydroxide,  
19 potassium hydroxide, sodium silicate, potassium silicate, sodium metasilicate, potassium  
20 metasilicate, sodium phosphate, sodium dihydrogen phosphate, ethanolamine or mixtures of  
21 such chemicals. Surfactants are also added to the developer and include such anionic surfactants  
22 as sodium alkylbenzenesulfonates, sodium alkynaphthalenesulfonates and sodium  
23 dialkylsulfosuccinates at concentrations from about 0.003 to 3 percent by weight.

1        In this invention, the use of positive plates together with their respective developers is  
2        highly desirable and advantageous. Positive plates have outstanding stability; some such plates  
3        have a shelf-life of more than two years when stored at room temperature. They also have  
4        excellent resolution and produce images that have a long press-life that is greatly extended by a  
5        bake process when heated at about 250 to 280C for about 1 to 3 minutes. The image reversal  
6        process doesn't detract from these properties. The developers used on the positive plates are  
7        ecologically acceptable; they don't contain any undesirable volatile organic chemicals.

8        The following non-limiting examples serve to illustrate the invention.

9        EXAMPLE 1

10       Prepare a solution of 29.6 grams Alnovol PN-430, a cresol formaldehyde novolac resin  
11       available from Hoechst in 308 grams ethyl lactate. To 50 grams of this solution, add 2.7 grams  
12       of Positive Diazo LL, a naphthoquinone-1,2-(diazide-2)-5-sulfonic acid ester available from  
13       Molecular Rearrangement Inc. of Newton, NJ ( MRI ) which is made by the reaction of  
14       naphthoquinone-1,2-(diazide-2)-5-sulfonyl chloride with 2,2'-thiobisnaphthol. In this reaction,  
15       mono and sulfonic acid esters can form. The molar ratio of the two reactants in the manufacture  
16       of Positive Diazo LL is adjusted so that the product that is produced is a mixture of 60%  
17       disulfonic acid ester and 40% monosulfonic acid ester. The solution is coated onto a grained,  
18       anodized and silicated aluminum sheet using a number 10 wire wound rod followed by drying  
19       with a hot air dryer. The entire plate is blanket exposed to 20 units of light using the high  
20       intensity setting of a Magnum Platemaker. Microdrops of 1% aqueous solutions of sodium  
21       metasilicatepentahydrate and sodium carbonate together with a 1% solution of triethanolamine in  
22       a solvent mixture of 25 parts acetone and 75 parts water are then applied. The treated coating is

1 then heated for 10 minutes at 110C followed by development with an alkaline solution of the  
2 following composition:

3           Sodium metasilicatepentahydrate                         55 grams

4   (from the PQ Corp. under the name Pentabead 20)

5           Aerosol OS Surfactant from Cytec                         2.2 grams

6           Water   1000 ml

7       The parts of the coating where the drops are applied are insolubilized in the developer by the  
8       heat treatment. The other parts of the coating are still soluble in the developer after the heat  
9       treatment. During development, they are quantitively removed leaving the hydrophilically  
10      treated aluminum bare. Images are produced on the coated plate from the sodium carbonate and  
11      sodium metasilicate solutions that correspond to the size of the drops of the applied solutions.

12      Spreading of the triethanolamine solution occurs when it is applied onto the coating. It produces  
13      a larger image than the original size of the drops. The spreading of the drop is attributed to the  
14      presence of acetone in the solution.

15      The above-coated plate is a positive plate. When light exposed and developed in the usual  
16      manner without any chemical treatment, a positive image is produced.

17

## 18 EXAMPLE 2

19      In this example, a positive plate, commercially available from Lastra (Futoro-ORO) of  
20      Sulmona, Italy is evaluated. It is comprised of an o-naphthoquinone diazide -5-sulfonic acid  
21      ester and alkali soluble resins together with dyes and indicator dyes. The Lastra plate is blanket  
22      light exposed by the procedure used on the coating from Example 1. Drops of 1% sodium  
23      carbonate are applied onto the exposed plate followed by heating at 120C for 4 minutes. After

1 development by the alkaline developer solution used in Example 1, an excellent image is  
2 produced that corresponds to the size of the applied drops. During the heat treatment, the  
3 coating is only insolubilized where the sodium carbonate solution is applied.

4

5 EXAMPLE 3

6 This example describes image formation on the Lastra positive plate using Monazoline C,  
7 1-hydroxyethyl-2-cocoylimidazoline available from Uniqema in New Castle, DE.

8 Prepare the following solutions:

		A	B	C	D
10	Monazoline C	0.25g	0.25g	0.18g	0.09g
11	Isopropyl Alcohol	2.5g	7.5g	5.5g	4.5g
12	Glycerine	--	--	2.0g	4.5g
13	Water	8g	62.5g	22.5g	45g

14 A Lastra positive plate is blanket light exposed by the procedure used on the coating from  
15 Example 1. Drops of the solutions A through D are applied onto the coating. Parts of the  
16 coating where solution:

- 17 1. A is applied are heated at 120C for 1 minute,
- 18 2. B is applied are heated at 105C for 45 seconds and also at 95C for 1 minute,
- 19 3. C is applied are heated at 95C for 1 minute and
- 20 4. D is applied are heated at 95C for 30 seconds and also at 70C for 1 minute.

21 After development by the alkaline developer described in Example 1, excellent images are  
22 produced by the four solutions on all the plates that are differently heat treated. When the  
23 imaged plates are treated with water and then rubbed with a webril wipe that is saturated with

1 water and a lithographic ink, the images are inked while the aluminum in the non- imaged areas  
2 don't absorb any ink. This example illustrates that image formation takes place from solutions  
3 of Monazoline C over a wide concentration range and that the time and temperature of the  
4 heating step are also over a wide range.

5

6 EXAMPLE 4

7 This example illustrates image formation using Monazoline C Acetate, which is prepared  
8 by the addition of acetic acid to an aqueous dispersion of Monazoline C. Prepare the following  
9 solutions:

	A	B	C
11 Monazoline C	0.3	0.3g	0.3g
12 Water	60ml	60ml	60ml
13 Acetic Acid, 3.4%	1.0g	1.7g	2.1g

14 The pH of Solutions A, B and C is 10, 7 and 5, respectively. The pH of the Monazoline  
15 C solution without the addition of acetic acid is 11. Monazoline C Acetate is water soluble and  
16 upon the addition of acetic acid, Monazoline C is solubilized. The Lastra positive positive plate  
17 is blanket light exposed by the procedure described in Example 1. Drops of the three solutions  
18 are applied onto the plate and then heated at 100C for 1 minute. After development with the  
19 alkaline developer, excellent images are produced where the drops are applied that correspond to  
20 the size of the applied drop. The images were unaffected by rubbing vigorously with a webril  
21 wipe that is wet with the alkaline developer and is indicative of its excellent adhesion and  
22 chemical resistance. The low pH of Solution C is an indication that in addition to the formation

1 of the acetate salt of the imidazoline, some unreacted acetic acid is present which doesn't detract  
2 from its decarboxylating properties.

3

4 EXAMPLE 5

5 This example illustrates image formation on the Lastra positive plate using  
6 triethanolamine. Prepare a solution of:

7 Triethanolamine 0.3g  
8 Isopropyl Alcohol 3g  
9 Water 62g

10 Apply the solution onto the blanket light exposed plate and after heating at 110C for 2  
11 minutes followed by development in the usual manner, satisfactory images are produced where  
12 the drops are applied.

13

14 EXAMPLE 6

15 This example illustrates image formation using imidazole. Prepare a solution of:

16 Imidazole from BASF 3g  
17 Ethanol 10g  
18 Water 90g

19 Apply the solution onto a blanket light exposed Lastra plate and then heated at 90C for  
20 90 seconds followed by alkaline development. Satisfactory images are produced where the  
21 solution is applied. The pH is 8.5 for the 1% imidazole solution.

22

23

## 1 EXAMPLE 7

2 This example illustrates image formation with Monazoline O and T and the evaluation of  
 3 three other commercially available positive plates based on naphthoquinone-1,2-(diazide-2))-5-  
 4 sulfonic acid esters, Capricorn DH from KPG in Norwalk, CT; Steinbacher Elan SP 123 from  
 5 Steinbacher Polymer GMBH in Germany and the Inkker positive plate from Inkker Systems  
 6 Corp. in Seoul, Korea. Prepare solutions:

		A	B	C
8	Monazoline T, Tall Oil Hydroxyethyl Imidazoline, from Uniqema	0.2g	--	--
10	Monazoline O, Oleyl Hydroxyethyl Imidazoline, from Uniqema	--	0.2g	--
12	Monazoline C	--	--	0.4g
13	Ethyl Lactate	4g	3g	--
14	Glycerin	2g	2g	--
15	Water	25g	25g	25g
16	Acetic Acid, 3.4%	--	--	1.5g

17 All three plates are blanket light exposed to 20 units of light from the high intensity  
 18 setting of the Magnum Platemaker. Drops of solutions A and B are applied onto the KPG and  
 19 Steinbacher plates which are then heated at 105C for 1 minute followed by development with the  
 20 dilute aqueous alkaline solution used in Example 1. On both plates the only areas where the  
 21 coating was insoluble and remained on the plate was where the drops were applied. Excellent  
 22 images are produced that correspond to the size of the applied drops. The unexposed coating is  
 23 completely removed leaving the aluminum hydrophilic in those areas.

1       Drops of solution C are applied onto the Inkker plate that is then heated at 105C followed  
2       by development as previously described in this example. Excellent images are produced where  
3       the drops are applied and in the other areas the coating is completely removed leaving the  
4       aluminum hydrophilic.

5

6       EXAMPLE 8

7       This example illustrates image reversal of positive plates using isostearyl ethylimidonium  
8       ethosulfate available from Uniqema Corp.under the name Monoquat ISIES and evaluates a  
9       positive plate made with the same ingredients as the one described in example 1 except that it  
10      contains two additional ingredients, a dye and an indicator dye. Prepare a solution of:

11	Ethyl Lactate	44g
12	Diazo LL	2.69g
13	Alnovol PN-430	4.32g
14	Victoria Blue Dye	0.07g
15	Sudan M Yellow 150 from BASF	0.07g

16      which is coated onto a grained, anodized and silicated sheet of aluminum using a number 10  
17      wire wound rod and dried with a hot air blower. Prepare solutions of:

	A	B
19	Monoquat ISIES	0.40g
20	Monazoline C	--
21	Isopropyl Alcohol, 70%	0.25g
22	Ethyl Lactate	4g
23	Glycerin	--
		3g
		0.75g
		2g

1 Water 25g 25g

2 The pH of Solution A is 6.5. After blanket light exposure of the positive plate, apply drops of  
3 solutions A and B and then heat for 1 minute at 105C. The coating is insolubilized where the  
4 drops are applied. After development by the alkaline developer, excellent images are produced  
5 and the aluminum in the non-imaged areas is hydrophilic. Drops of solution A are also applied  
6 to a blanket light exposed positive plate of Inkker Systems Corp. which after heating at 105C for  
7 1 minute followed by development with the alkaline developer produce excellent images. The  
8 only areas of the coating that are insoluble in the developer are where the drops are applied.

9

10 EXAMPLE 9

11 This example illustrates image formation using an amino amide and its corresponding  
12 acotate that are produced from Monazoline C, coycoyl hydroxyethyl imidazoline. In the  
13 presence of water Monazoline C and its acetate salt will gradually hydrolyze to produce an  
14 amino amide and an acetate salt, respectively. Prepare solutions of:

	A	B
16 Monazoline C	0.2g	0.25g
17 Ethyl lactate	--	3g
18 Glycerine	--	0.75g
19 Water	40g	25g
20 Acetic Acid, 3.4%	1.4g	--

21 The two solutions are stored at room temperature for two months and within this period  
22 hydrolysis is believed to occur to produce the amino amide and amino amide acetate. Drops of  
23 the two solutions are applied onto the blanket light exposed positive plates of the one prepared in

1 Example 8 and of the Inkker Systems Corp. They are then heated at 105C for 1 minute followed  
 2 by development with the alkaline developer. Excellent images are produced where the drops are  
 3 applied and in the other areas the coating is readily removed.

4

5 EXAMPLE 10

6 This example illustrates image reversal of positive plates using the sulfate and phosphate  
 7 salts of Monazoline C and using Witcamine TI-60, tall-oil fatty acid-diethylenetriamine  
 8 imidazoline, ethoxylated available from the Crompton Corporation. The Lastra positive plate is  
 9 blanket light exposed as previously described. Prepare solutions of:

	A	B	C	D	E
11 Monazoline C	0.23g	0.23g	0.23g	0.23g	--
12 Witcamine TI-60	--	--	--	--	0.5g
13 Water	40ml	40ml	40ml	40ml	50ml
14 Sulfuric Acid, 3.4%	1g	1.4g	--	--	--
15 Phosphoric Acid, 3.4%	--	--	1g	1.6g	--
16 pH	8	4	8.5	4	8.3

17 Drops of the five solutions are applied onto the blanket exposed Lastra plate, which is then  
 18 heated at 110C for 2 minutes followed by development by the dilute aqueous alkaline developer.  
 19 The coating is only insoluble in the developer where the drops are applied. On development,  
 20 excellent images are produced. A 3.4% aqueous solution of phosphoric acid containing 10%  
 21 ethanol when applied onto the blanket light exposed Lastra plate followed by heating at 110C for  
 22 3.5 minutes didn't insolubilize the coating in the dilute aqueous developer. This indicates that  
 23 the phosphoric acid that is present in Solution D is not insolubilizing the Lastra plate.

## 1 EXAMPLE 11

2 This example illustrates image reversal using N-acetylenediamine and its acetate  
 3 salt. Prepare solutions of:

	A	B
5 N-acetylenediamine	0.22g	0.22g
6 Glycerine	1g	1g
7 Isopropyl alcohol, 70%	4g	4g
8 Ethyleneglycol monobutyl ether	0.22g	0.22g
9 Glycerine	1g	1g
10 Isopropyl alcohol, 70%	4g	4g
11 Ethyleneglycol monobutyl ether	0.4g	--
12 Acetic acid, 3.4%	--	2.6g

13 The pH of Solutions A and B are 10.5 and 8.5, respectively. After blanket light exposure of the  
 14 Lastra positive plate, apply drops of the two solutions followed by heating the plate at 110C for  
 15 4 minutes. Excellent images are formed on development where the drops are applied. The non-  
 16 chemically treated parts of the coating are readily dissolved in the alkaline developer.

17

## 18 EXAMPLE 12

19 This example illustrates the use of a positive plate in the image reversal process that is made  
 20 with an o-naphthoquinone-1,2-(diazide-2)-4-sulfonic acid ester. Prepare a solution of:

21 Alnovol PN-430	4.32g
22 2,1,4 Diazo Ester D-42 from MRI, CAS# 80296-78-2	2.69g
23 Ethyl Lactate	44g

1	Victoria Blue Dye	0.085g
2	Sudan M Yellow 150	0.070g

3 The solution is coated onto a grained, anodized and silicated aluminum sheet using a number 10  
4 wire wound rod followed by drying with a hot air dryer. Drops of the phosphate salt of  
5 Monazoline C which is Solution B of Example 10 is applied onto this plate that is blanket light  
6 exposed in the previously described manner followed by heating at 60C for both 15 and 30  
7 seconds. Where the drops are applied, the coating is insoluble while the non-chemically treated  
8 coating is soluble in the dilute aqueous alkaline developer solution prepared in Example 1. On  
9 development, an image forms where the drops are applied and the coating is quantitatively  
10 removed in the unimaged areas leaving the hydrophilically treated aluminum bare. This  
11 example is the only one that uses a naphthoquinone-1,2-(diazide-2)-4-sulfonic acid ester instead  
12 of -5-sulfonic acid esters. Such coatings decarboxylate at lower temperatures both when  
13 chemically and non-chemically treated. For example, when the coating prepared in this example  
14 is heated at 80C for only 30 seconds, it is insolubilized in the developer.

15

16 On-Press Developable Plate

17 In another aspect of the invention, the method for preparing an on-press developable  
18 plate for printing comprises the steps of:

- 19     a) providing an on-press developable plate;
- 20     b) applying imagewise an insolubilizing chemical to the plate coating;
- 21     c) heating the plate;
- 22     d) mounting the plate on the plate cylinder of a conventional offset lithographic press;
- 23     e) operating the press such that the press working fluids are applied to the plate coating.

1       A variety of photopolymer chemistries can be used to create on-press developable  
2       coatings for lithographic plates. Often such plate coatings comprise acrylate monomers such as  
3       benzyl acrylate, benzyl methacrylate, butoxyethyl acrylate, butoxymethyl methacrylate,  
4       cyclohexyl acrylate, cyclohexyl methacrylate, 2-hydroxyethyl acrylate, 2-hydroxyethyl  
5       methacrylate, glycidyl acrylate, glycidyl methacrylate, methyl methacrylate, ethyl methacrylate,  
6       butyl methacrylate, phenoxyethyl acrylate, phenoxyethyl methacrylate, phenyl methacrylate,  
7       ethyleneglycol diacrylate, ethyleneglycol dimethacrylate, diethyleneglycol diacrylate,  
8       diethyleneglycol dimethacrylate, triethyleneglycol diacrylate, triethyleneglycol dimethacrylate,  
9       tetraethyleneglycol diacrylate, tetraethyleneglycol dimethacrylate, polyethyleneglycol diacrylate,  
10      polyethyleneglycol dimethacrylate, neopentylglycol diacrylate, neopentylglycol dimethacrylate,  
11      ethyleneglycolbisglycidyl diacrylate, ethyleneglycolbisglycidyl dimethacrylate,  
12      trimethylolpropane triacrylate, trimethylolpropane trimethacrylate, glycerol diacrylate, glycerol  
13      dimethacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, and pentaerythritol  
14      tetramethacrylate. Such plate coatings typically also comprise photoinitiators such as 2,2-  
15      dimethoxy-2-phenylacetophenone, benzophenone, benzil and its ketals, ketocoumarin, xanthone,  
16      anthraquinones, tris[4-(dimethylamino)phenyl]methane, benzoin, and benzoin ethers.

17       Such plate coatings are well known in the art and are described in U.S. Pat. Nos.  
18      5,514,522; 5,516,620; 5,556,924; 5,599,650; 5,607,816; 5,677,108; 5,677,110; 5,795,698;  
19      5,811,220; 5,997,993; 5,620,822; 5,910,395; 5,925,497; 5,849,462; and 6,027,857 incorporated  
20      herein by reference. Commercially available on-press developable plates include the KemFre  
21      from Spectratech of Wake Forest, North Carolina, and the most preferred DirectPrint from KPG  
22      of Norwalk, Connecticut. The DirectPrint plate coating comprises acrylate monomers such as  
23      pentaerythritol triacrylate and free radical photoinitiators such as 2-isopropylthioxanthone

1 (Quanticure available from Biddle Sawyer, New York) and tris[4-  
2 (dimethylamino)phenyl]methane (Crystal Violet leucobase). The DirectPrint plate coating does  
3 not contain substantial carboxylic acid functionality such that an esterification reaction could  
4 result in image-worthy insolubilization.

5 In the invention described hereinabove the plate coatings comprise photosensitive free  
6 radical initiators so that the insolubilization reaction can be initiated by light exposure. In  
7 another aspect of the invention, a proprietary polymer plate coating can comprise acrylate  
8 monomers and free radical initiators as described hereinabove. However, it may be desired to  
9 manufacture a proprietary plate coating optimized for the process of imaging by chemical  
10 insolubilization. In such a proprietary coating, it would be advantageous to use  
11 nonphotosensitive free radical initiators such as organic or inorganic peroxides or azos so that  
12 the user need not be concerned about incidental light exposure. Suitable peroxide initiators  
13 include dicumyl peroxide, 2,5-dimethyl-2,5-di(tbutylperoxy)hexane, di-t-butyl peroxide, t-  
14 butylperoxy benzoate, 2,5-dimethyl-2,5-di(t-butylperoxy)hexane-3 and lauryl peroxide. Suitable  
15 azo free radical initiator compounds include azoisobutyronitrile and dimethylazoisobutyronitrile,  
16 and azo-bis-4-cyano-pentoic acid.

17 As an alternative to using nonphotosensitive free radical initiators, photoinitiators that  
18 require co-synergists can be used to produce nonphotosensitive coatings by incorporating only  
19 the photoinitiator together with acrylic monomers in a coating. The coating then can be  
20 chemically imaged by the imagewise application of a co-synergist that would initiate the  
21 polymerization reaction in a subsequent heat treatment step. Illustrative of some such systems  
22 are: a 2,4,5-triphenylimidazoyl dimer consisting of two lophine radicals bound together by a  
23 single covalent bond as the photoinitiator, and a free radical producing hydrogen donor or an

1 active methylene compound and a p-aminophenyl ketone as co-synergists as described in U.S.  
2 Pat. Nos. 3,479,185 and 3,615,567 respectively, incorporated herein by reference, and the use of  
3 tertiary amines as co-synergists with thioxanthone photoinitiators as reported in Eur. Polym. J.  
4 No. 10, 841 (1985) incorporated herein by reference.

5 For photopolymer plates including on-press developable plates such as described above,  
6 the insolubilizing agent comprises pH-elevating agents typically of low molecular weight such  
7 as sodium carbonate, sodium bicarbonate, lithium carbonate, lithium hydroxide, sodium  
8 hydroxide, potassium hydroxide, sodium tetraboratedecahydrate, sodium  
9 pyrophosphatedecahydrate, sodium phosphate, sodium metasilicate, or amines such as  
10 ethanolamine, diethanolamine, triethanolamine, ethylamine, propylamine, butylamine,  
11 imidazolines, substituted imidazolines such as 1-hydroxyethyl-2-cocylimidazoline, 1-  
12 hydroxyethyl-2-caprylimidazoline, 1-hydroxyethyl-2-oleylimidazoline, and 1-hydroxyethyl-2-tall  
13 oil imidazoline, tall-oil fatty acid-diethylenetriamine imidazoline, imidazoles, substituted  
14 imidazoles, amino amides, aromatic amides, polyamines, or mixtures of such chemicals. The  
15 insolubilizing agent typically comprises from 0.1 to about 7.5 percent of the fluid. The pH range  
16 of the imaging fluid is between 7.5 and 13.5, and more preferably from about 8.0 to 12.5.

17 A most preferred insolubilizing fluid consists of 1% poly(ethylenimine) ( $M_w = 25,000$ ;  
18  $M_n = 10,000$ ) available from Aldrich, 98.9% water, and 0.1% of the surfactant FS-80 available  
19 from Air Products. After imagewise application of the insolubilizing fluid by IJP, it is most  
20 preferred to convectively heat the plate for about 60s at about 120C, taking care not to  
21 excessively expose the plate to ambient light. The plate is then ready to be mounted on press,  
22 developed according to standard procedure, and used for printing.

1       Because of their high aqueous solubility and their effectiveness at low concentrations, it  
2    is possible to formulate insolubilizing fluids with polyethylenimines that are both long-term  
3    shelf stable and long-term compatible with ink jet printhead materials and components. Without  
4    being bound by theory, it is believed that primary and secondary amines such as the  
5    polyethylenimines act as a co-synergists in conjunction with the 2-isopropylthioxanthone  
6    photoinitiator of the DirectPrint plate to reduce the thermal stability of the coating in the imaged  
7    areas. Thus crosslinking of the plate coating occurs exclusively in the imaged areas during the  
8    convective heating step.

9           The following non-limiting examples serve to further illustrate the invention.

10    EXAMPLE 13

11       A marking fluid was mixed with the following components: 98.90 g of distilled water, 1.00  
12    g of poly(ethylenimine) ( $M_w = 25,000$ ;  $M_n = 10,000$ ), and 0.10 g of FS-80 surfactant (Air  
13    Products and Chemicals). This solution was injected into an ink cartridge and charged into an  
14    Epson 3000 printer. An image was jetted onto a KPG DirectPrint plate, which was then baked in  
15    an oven at 230°F for 3 minutes. The plate was mounted on a rotary offset press, developed  
16    according to the manufacturer's instructions and used to print black ink on standard copier paper  
17    stock. 900 images were printed with no evidence of plate wear. The image was clean, the lines  
18    clear, and the individual image dots were undamaged. Dot diameters on the plate averaged ~ 54  
19     $\mu\text{m}$ . Dot diameters on paper averaged ~ 80  $\mu\text{m}$ . Alternatively, a DirectPrint plate so imaged was  
20    passed through a convection conveyor oven set at 260°F for an exposure time of 90 seconds.  
21    Press results were similar.

1 That hundreds of impressions with good image quality can be obtained from a chemically  
2 insolubilized negative working PS plate without a baking step after development is a unique and  
3 surprising result.

4  
5 EXAMPLE 14  
6

7 A marking fluid analogous to that described in Example 13 was mixed, except that the  
8 polyethylenimine had a number average molecular weight (Mn) of 600. A KPG DirectPrint  
9 plate was processed in the exact same way as in Example 13. This also yielded durable images  
10 when developed on press with black ink; no wear was observed after 100 impressions. The dots  
11 on both the plate and the paper were about 25% larger than those in Example 1, and the resulting  
12 images were thus much darker.

13  
14 EXAMPLE 15

15 A marking fluid was prepared as in Example 13, except that the polyethylenimine had an Mn  
16 = 423. The plate was imaged with this fluid and then heated in the exact same way as in  
17 example 13. This also yielded durable images when developed on press with black ink. No  
18 wear was observed after 100 impressions. The dots on both the plate and the paper were about  
19 25% larger than those in Example 13, and the resulting images were thus much darker. It is  
20 believed that the high average molecular weight of the polyethyleneimine polymer in Example  
21 13 inhibits the insolubilizing agent from spreading through the coating during the heating step  
22 and thus facilitates the desired small dot size.

23  
24  
25

## 1 EXAMPLE 16

2 A marking fluid was mixed with the following components: 98.90 g distilled water, 1.00 g  
3 pentaethylenehexamine, and 0.10 g FS-80 surfactant. A KPG DirectPrint plate was imaged with  
4 this fluid and heated similar to Example 13. This yielded good images when developed on press  
5 with black ink. The dot size on the paper was ~ 100 µm.

6

## 7 EXAMPLE 17

8 A marking fluid was mixed with the following components: 69.50 g distilled water, 5.00 g  
9 glycerine, 25.00 g diethylene glycol, and 0.50 g pentaethylene hexamine. This solution was  
10 injected into an ink cartridge and charged into an Epson 3000 printer. An image was jetted onto  
11 a KPG DirectPrint plate, which was then baked at 230°F for three minutes. The plate was  
12 transferred to a rotary offset press, developed according to the manufacturer's directions, and  
13 used to print black ink on standard copy paper stock. 100 prints were produced with little or no  
14 sign of degraded image wear. This was typical performance of marking fluids employing the  
15 lower molecular weight oligomers of ethylenimine.

16

## 17 EXAMPLE 18

18 Marking fluids were mixed with the following components: 20.00 g distilled water, 1.00 g of  
19 Ancamide 50X (X = 0, 1, 2, 3, or 7) which are available from Air Products, 2.40 g ethyl lactate,  
20 and 0.55 g glycerine. Each of these fluids was pipetted down in small drops on separate areas of  
21 a KPG DirectPrint plate, which was then baked at 230°F for 15 minutes. This plate was  
22 transferred to a rotary offset press and used to print black ink on standard copy paper stock.

1    1000 prints could be generated with little or no sign of degradation or wear of the dots for each  
2    of the Ancamide chemicals tested.

3

4    EXAMPLE 19

5       A marking fluid was mixed with the following components: 100.00 g distilled water, 5.00 g  
6    of Ancamide 500 (Air Products and Chemicals), 12.00 g ethyl lactate, and 2.75 g glycerine. This  
7    solution was used analogously to Example 16 in producing an image on a KPG DirectPrint plate,  
8    which was then baked at 230°F. for 15 minutes, then transferred to a rotary offset press,  
9    developed, and used to print black ink on standard copy paper stock. 100 to 300 prints could be  
10   produced with little or no sign of degraded image wear. Large dots (> 100µm) were printed on  
11   the paper. This experiment was repeated with Ancamides 501, 502, 503, and 507; all resulted in  
12   similarly durable images.

13

14   EXAMPLE 20

15       A marking fluid was mixed with the following components: 100.00 g distilled water, 1.00 g  
16   Monazoline C (from Uniqema), 12.00 g ethyl lactate, and 2.75 g glycerine. Similar fluids were  
17   also mixed with Monazoline O, and Monazoline T in place of the Monazoline C. Each of these  
18   fluids was pipetted down in small drops on separate areas of a KPG DirectPrint plate, which was  
19   then baked at 225°F for five minutes. The plate was transferred to a rotary offset press,  
20   developed, and used to print black ink on standard copy paper stock. The fluids containing  
21   Monazoline C, O, and T all produced good images in excess of 100 impressions.

22

23

1    EXAMPLE 21

2       A marking fluid was mixed with the following components: 87 g distilled water, 1 g  
3       Monazoline C, 5 g butyldiglycol, and 7 g glycerine. An image was jetted down onto a KPG  
4       DirectPrint plate, which was then baked at 230°F for three minutes. The plate was transferred to  
5       a rotary offset press, developed, and used to print black ink on standard copy paper stock.  
6       Images with sharp solids and good dot definition were produced.

7

8       Proprietary Plates

9       In this aspect of the invention, it is not necessary to use a commercially available or  
10      presensitized plate. Instead, the only requirement is that the plate has a press-worthy oleophilic  
11      coating that is soluble to a developer and that a jettable insolubilizing fluid can be developed for  
12      it.

13       Similar to the embodiment of the invention above-described in which positive plates  
14      comprised of quinone diazide sulfonic acid esters and alkali soluble resins are blanket exposed  
15      producing carboxylic acids which are then decarboxylated by imagewise application of an  
16      insolubilizing fluid according to the invention, it is possible to make a proprietary plate coating  
17      comprised of decarboxylatable carboxylic acids and alkali soluble resins but without any  
18      expensive o-quinone diazides. Such a coating should have all the desirable features of the  
19      positive plates according to the embodiment above-described, but would not be photosensitive  
20      and would also have a very long, even unlimited, shelf life. There would also be no need for the  
21      above-described blanket exposure step, and because o-quinone diazides are not present, the  
22      heating step can be performed at a higher temperature than is possible with commercial positive  
23      plates.

The decarboxylation reaction is represented by:



3 The reaction is favored if R contains electron withdrawing groups, three membered rings  
4 adjacent to the carboxyl group and beta, gamma double bonds, and is catalyzed by both acids  
5 and bases which can be incorporated in an insolubilizing fluid applied imagewise. Illustrative of  
6 the compounds that undergo decarboxylation are depicted in Structures 1 – 12. The compounds  
7 depicted in Structures 11 and 12 are formed by photodecomposition of their corresponding  
8 napthoquinone-1,2-(diazide-2)-sulfonic acid esters which are depicted respectively in Structures  
9 13 and 14.

10 The following non-limiting example serves to further illustrate this aspect of the invention.

## 11 EXAMPLE 22

12 Plate Coating

13 Prepare a solution of:

14	Alnoval PN-430	3.2g
15	2-Benzoylbenzoic acid	2.1g
16	(from Aldrich)	.
17	Victoria Blue Dye	0.06g
18	Sudan M Yellow 150	0.06g
19	Ethyl Lactate	33g

20 Which is coated onto a grained, anodized, and silicated aluminum sheet using a #10 wire wound  
21 rod followed by drying with a hot air dryer.

## 22 Insolubilizing Fluid Candidates

23 Prepare solutions A – E as follows:

		A	B	C	D	E
2	Isopropyl alcohol	--	2.5g	0.5g	--	--
3	2-Isopropoxyethanol	--	2.5g	5.0g	--	--
4	Water	80g	45g	33g	45g	49g
5	Sulfuric Acid, 96%	20g	5g	1g	--	--
6	2-Hydroxy-4-methoxy-					
7	benzophenone-5-sulfuric acid	--	--	--	5g	1.25g
8	(from Syntase)					
9	Surfynol 465	--	--	--	1drop	1drop

10       Drop of solutions A – E were applied onto the coated plate. The plate was then heated at  
 11      145C for 4 minutes. Upon development with a dilute aqueous solution similar to that described  
 12      in Example 1, satisfactory images were produced.

13       If the coating of this example contained typical o-quinone diazides, it would not be possible  
 14      to heat the plate to 145C for a substantial period without fogging (thermally insolubilizing) the  
 15      plate. Thus a process for chemical insolubilization of a non-photosensitive coating following by  
 16      a heating step presents unique and surprising advantages.

17       In another aspect of the invention, it is well known in the art that amines can act as epoxy  
 18      hardeners. In an embodiment of the invention above-described it is taught how to make a  
 19      jettable, stable fluid with effective amine hardeners such as the Ancamides and  
 20      polyethylenimines. Thus according to another aspect of the present invention, it is possible to  
 21      use such an insolubilizing fluid in conjunction with a plate coating comprised of epoxy  
 22      monomers.

23       The following non-limiting example serves to further illustrate the invention.

## 1 EXAMPLE 23

2 1 g of EPON 1031, 8 g of methylcellosolve, and 3 g isopropyl alcohol were mixed and  
3 heated to make a clear solution. EPON 1031 is a multifunctional  
4 epichlorohydrin/tetraphenolethane epoxy resin from Shell Chemicals. The solution was coated  
5 onto silicated aluminum plate to create an epoxy emulsion coating.

6 1% (by weight) aqueous polyethylenimine ( $M_n = 10,000$ ;  $M_w = 25,000$ ) was applied to this  
7 emulsion with a pipet in drops. The plate was then heated to 230 F for one minute and  
8 developed with SD-100 developer (Precision Lithograining), producing an image of the dots that  
9 is believed to be due to the cross linking of the epoxy by the polyethylenimine. Similarly it is  
10 known that polyamines and polyamine-functionalized compounds can be effective in directly  
11 cross linking resins comprising acid anhydrides or isocyanates.

12 In another aspect of the invention, it is possible to incorporate imagewise chemical  
13 insolubilization into a computer-to-press system. The essential elements of the press in this  
14 embodiment of the invention are shown in Fig. 5. A conventional offset lithographic press has  
15 dampening rollers 60 and inking rollers 64, which in normal operation, supply water-based  
16 dampening fluid 62 and ink 66 to a printing plate mounted on a plate cylinder 68. In normal  
17 printing operation, ink in the form of the image on the plate is transferred to the blanket cylinder  
18 70 and then to the paper that is conveyed through the press via the impression cylinder 72. In  
19 this embodiment, an unimaged on-press developable plate is mounted on the plate cylinder 68.  
20 It is then imaged with an insolubilizing fluid using an ink jet printhead 74 aligned to the plate  
21 cylinder 68. After imaging, if necessary to complete the insolubilization reaction, the plate can  
22 be heated in situ (not illustrated). Then the plate can be developed using the working fluids of  
23 the press and used in normal printing operation as above described.

1      The foregoing is exemplary and not intended to limit the scope of the claims that follow.

2